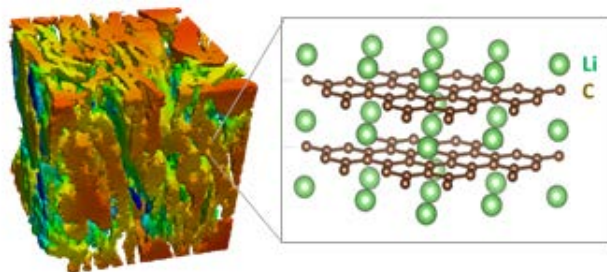BAT383
U.S. DEPARTMENT OF ENERGY
VEHICLE TECHNOLOGIES OFFICE ANNUAL MERIT REVIEW

X·CEL
eXtreme Fast Charge Cell Evaluation
of Lithium-ion Batteries

UNDERSTANDING IMPACT OF LOCAL HETEROGENEITIES DURING FAST CHARGE

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U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy
VEHICLE TECHNOLOGIES OFFICE

Argonne NATIONAL LABORATORY

SLAC

NREL

BERKELEY LAB

INL Idaho National Laboratory

Arlington, VA
June 10-13, 2019

OVERVIEW

Timeline

- Start: October 1, 2017
- End: September 30, 2021
- Percent Complete: 37%

Budget

- Funding for FY19 – $6,390k
  - ANL – $2,400k
  - NREL – $1,600K
  - INL – $440K
  - SLAC – $1,000K
 - LBNL – $950K

Barriers

- Cell degradation during fast charge
- Low energy density and high cost of fast charge cells

Partners

- Argonne National Laboratory (ANL)
- Idaho National Laboratory (INL)
- Lawrence Berkeley National Lab (LBNL)
- National Renewable Energy Laboratory (NREL)
- SLAC National Accelerator Lab
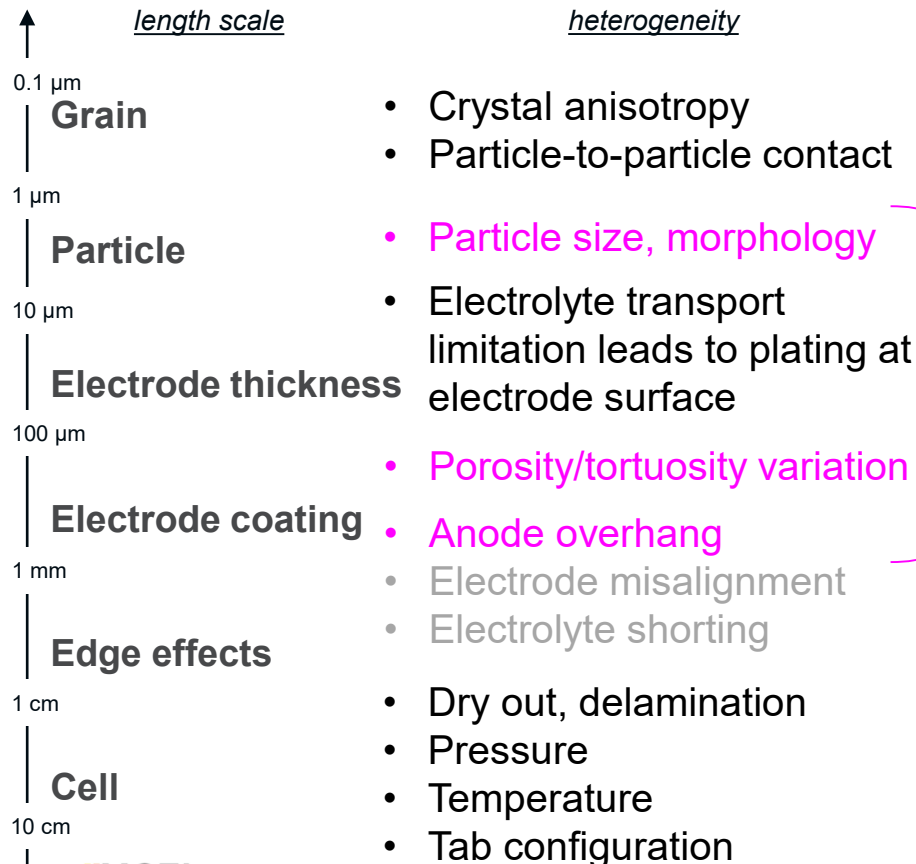
RELEVANCE – TRANSPORT LIMITATIONS

Transport limitations impact onset of lithium (Li) plating during fast charge

1) Li⁺ depletion in electrolyte
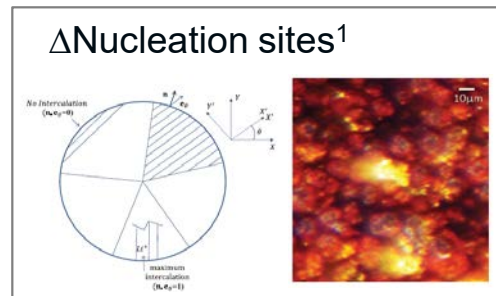
2) Li saturation @ graphite surface

Atomistic modeling
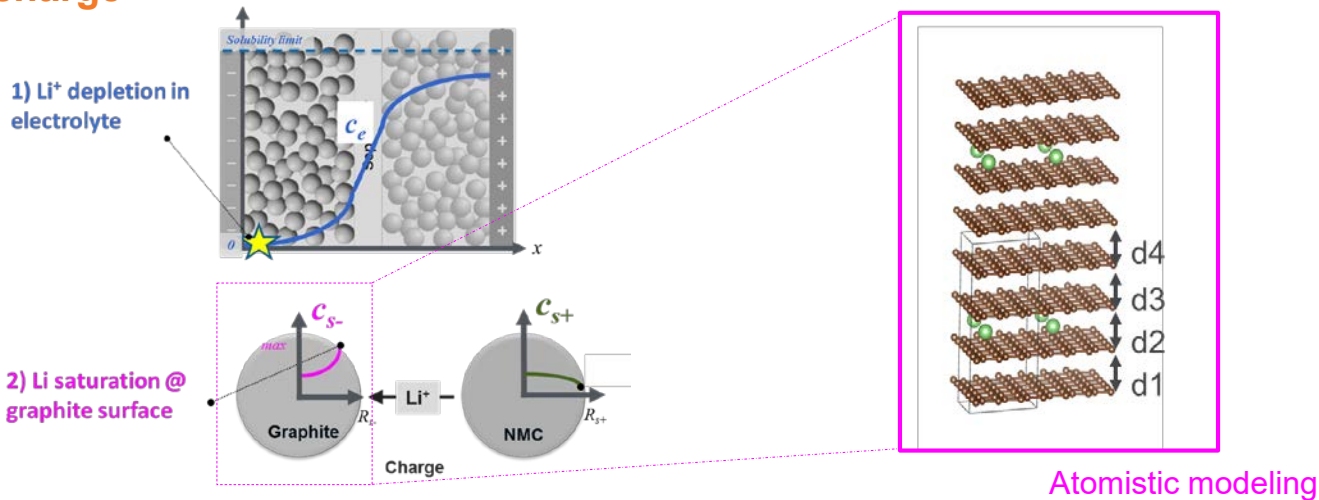
- When electrolyte Li⁺ ions become depleted in graphite electrode, only the front of the electrode is used (BAT371)

- Excessive charge rate at the front leads to graphite saturation and Li plating

- Experiments show solid diffusion in graphite improves with higher charge rates (BAT371)

- This phenomena needs to be better understood (this presentation)

RELEVANCE – HETEROGENEITIES

Heterogeneities at all length scales cause early onset of Li plating

length scale	heterogeneity	examples

length scale (axis, top = 0.1 µm, bottom = 10 cm)
- 0.1 µm — **Grain**
- 1 µm — **Particle**
- 10 µm — **Electrode thickness**
- 100 µm — **Electrode coating**
- 1 mm — **Edge effects**
- 1 cm — **Cell**
- 10 cm

heterogeneity
- Crystal anisotropy
- Particle-to-particle contact
- Particle size, morphology
- Electrolyte transport limitation leads to plating at electrode surface
- Porosity/tortuosity variation
- Anode overhang
- Electrode misalignment
- Electrolyte shorting
- Dry out, delamination
- Pressure
- Temperature
- Tab configuration

examples

ΔNucleation sites[1]

Main focus to date (this presentation)

Cell-scale heterogeneities[2]

Ira Bloom (ANL)

XCEL
eXtreme Fast Charge Cell Evaluation of Lithium-ion Batteries

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VEHICLE TECHNOLOGIES OFFICE

1. Harris et al. JES (2012)   2. Photo: Ira Bloom, ANL

OBJECTIVES

10-15 minute fast charge of high-energy, 15-year-life electric vehicle (EV) battery

- Aid XCEL team in the interpretation of fast-charge experiments
  - Explain apparent increase in Li diffusivity in graphite at high rates
  - Explain patterns of localized Li plating
  - Accurately predict onset of Li plating
    - Li is not always visible or detectable yet still contributes to capacity fade on fast charge)

- Use models as feedback to experiments and provide guidance on designs/requirements/strategies to
  - Improve fast charge acceptance
  - Suppress Li plating

FY19 MILESTONES

NREL Milestones (shared with BAT340)	Date	Status
Simulation-based comparison of electrochemical response of ANL graphite electrode library using 3D geometry obtained from tomography. Correlate heterogeneity of electrode utilization with electrode morphology.	Q1	Complete
Demonstrate first simulation cases predicting the onset of Li plating side reaction guiding future quantification of how active material heterogeneous utilization impacts degradation.	Q2	Complete
Rationalize performance and degradation experimental findings from NREL, ANL, and INL using models to explain underlying mechanisms behind observed electrochemical performance and degradation. (Go/No-go)	Q3	On track
Propose design guidelines for active material particle size, morphology, and composite electrode tortuosity, as well as advanced strategies/architectures that can help batteries achieve 10-minute charge.	Q4	On track

ANL Milestones	Date	Status
Use atomistic models to examine possible mechanisms for apparent increase of Li diffusion coefficient in graphite at higher rates.	Q4	On track

1) ATOMISTIC MODELING OF LI TRANSPORT IN GRAPHITE

APPROACH – ATOMISTIC MODELING

Spin-polarized density functional theory (DFT) as implemented in the Vienna Ab Initio Simulation Package (VASP).
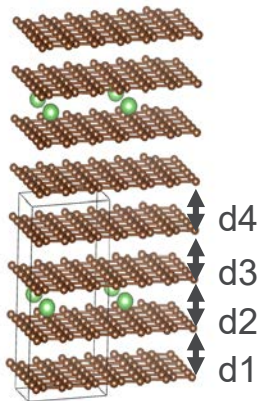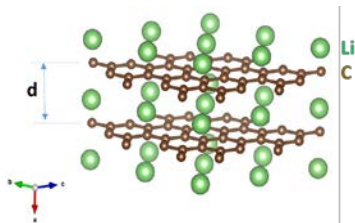
- The exchange-correlation potentials are treated by the generalized gradient approximation (GGA) parametrized by Perdew, Burke, and Ernzerhof (PBE).

- The interaction between valence electrons and ion cores is described by the projected augmented wave (PAW) method.

- The GGA+U (Hubbard potential correction) scheme is used for applying the on-site correlation effects among 3d electrons of the transition metals (TM).

- After geometry optimizations within the DFT+U framework, electronic relaxation was performed using a single point calculation with the hybrid functional HSE06.

- The Nudged Elastic Band (NEB) method was used to calculate the energy barrier for Li diffusion

ATOMISTIC MODELING

Is there a new mechanism of lithium diffusion in graphite during fast charge?
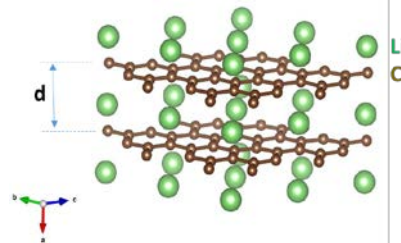
- Li diffusion in graphite has been measured at different charge states [1, 2, 3], and modeled using a combination of DFT, cluster expansion, and kinetic Monte Carlo techniques [4]. DFT-based modeling has also been performed to include some edge effects (edge defects, O and H terminated) [5].

- Existing models cannot explain recent data on fast charging

- New possible diffusion mechanisms and configurations will be investigated using DFT:

  1. **Effect of C-C spacing (d) and local Li concentration on the diffusion mechanism**

  2. **Effect of electronic configuration on the diffusion mechanism**

  3. Effect of defects (C vacancies, Stone-Wales, …) on the diffusion mechanism

1. Guo et al. *New Carbon Materials*, Vol. 22(1), 7-11 (2007)
2. Thomas-Alyea et al. *J. Electrochem. Soc.* 164(11) E3063-E3072 (2017)
3. Langer et al. *Phys. Rev. B* 88, 094304 (2013)
4. Person et al. *J. Phys. Chem. Lett.* 2010, 1, 1176–1180 (DOI: 10.1021/jz100188d)
5. Leggesse et al. *Carbon* 103 (2016) 209-216

GRAPHITE INTER-PLANAR DISTANCE DURING FAST CHARGING

LiC_{36}

**Assume at the beginning of the fast charge that there are more electrons than Li^+ ions.**
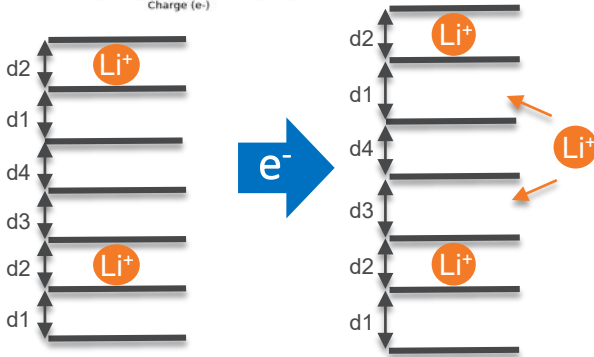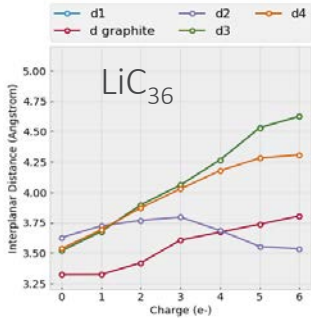
- For LiC_{36} the insertion of Li increases all the inter-planar distances. (no extra charge)

- Extra charge increases the inter-planar distances d1 and d3 (next to Li layer) more than any other channel

- The inter-planar distance d2 (where Li sits) decreases for excess electron charges between 4 and 10 (increased ionic character)

- The next more favorable stage would fill the channels next to Li, which is opposite to what happens in slow charge conditions

- Evidence of a different mechanism for graphite lithiation under fast charging conditions.

(a) 1st Stage   (b) 2nd Stage   (c) 3rd Stage   (d) 4th Stage

No extra electrons   3 extra electrons   6 extra electrons
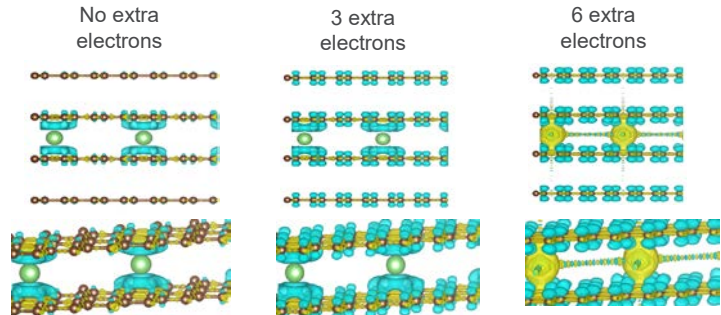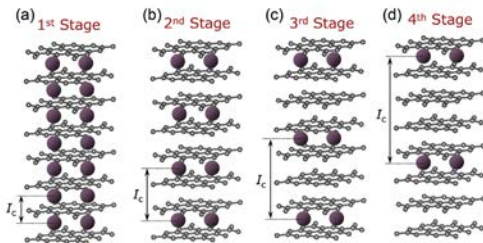
KINETICS DURING THE FAST CHARGING PROCESS

- The NEB method was used to calculate the energy barrier for Li diffusion

- A supercell with very dilute Li concentration (LiC_{72}) is used to investigate the effect of the presence of extra electrons in the system

- The energy barrier decreases when the number of extra electrons increases

- The decrease in the energy barrier for Li diffusion is consistent with the increase of the inter-planar distance
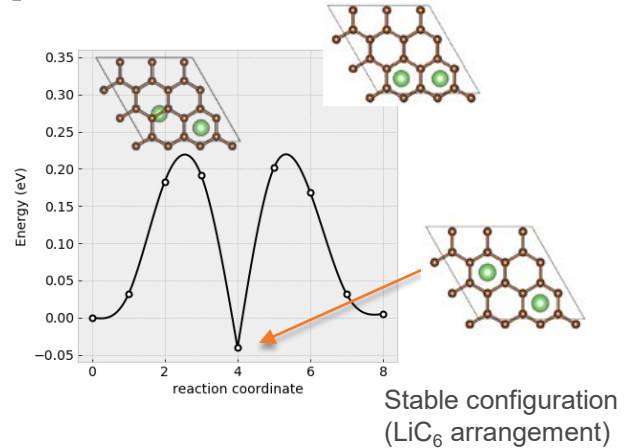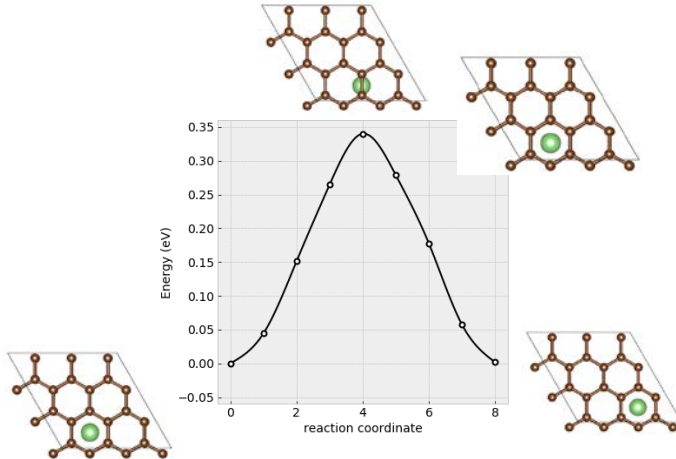
Change in energy along Li diffusion reaction coordinate
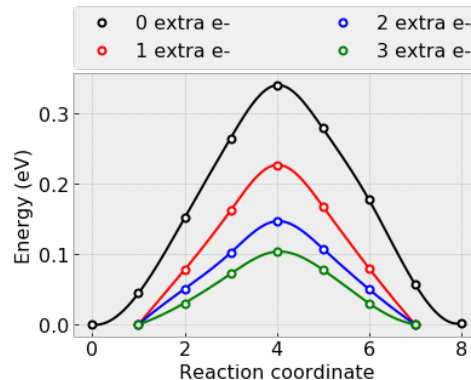
Energy barrier for Li diffusion as a function of extra electrons

CONCERTED LI DIFFUSION

Neutral System

Stable configuration
(LiC_6 arrangement)
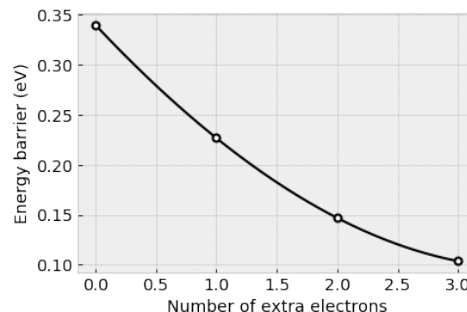
- The energy barrier for Li diffusion is reduced from 0.34 eV to 0.22 eV for high Li local concentrations (fast charge conditions)
- The energy barrier for Li diffusion is slightly reduced from 0.34 eV to 0.32 eV for first Li migration and to ~0.26 eV for the second Li migration (fast charge conditions)
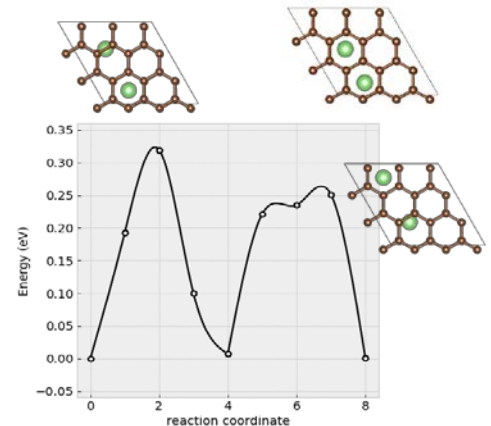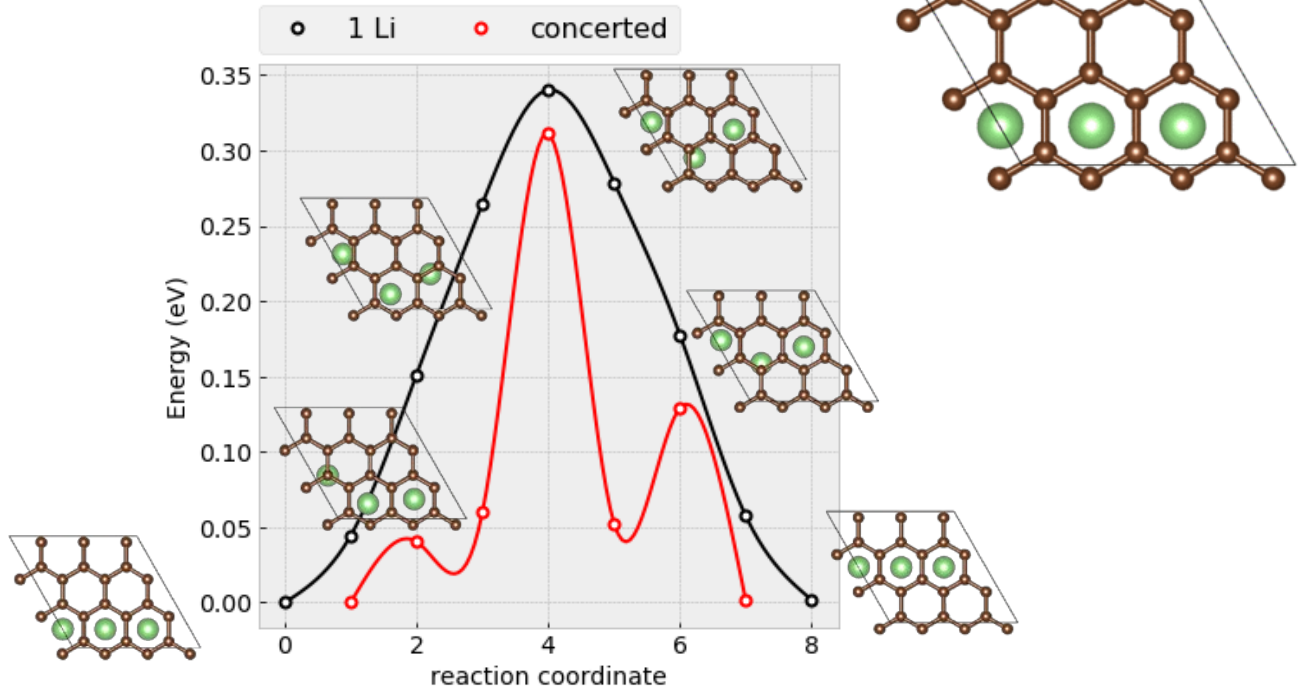
CONCERTED LI DIFFUSION
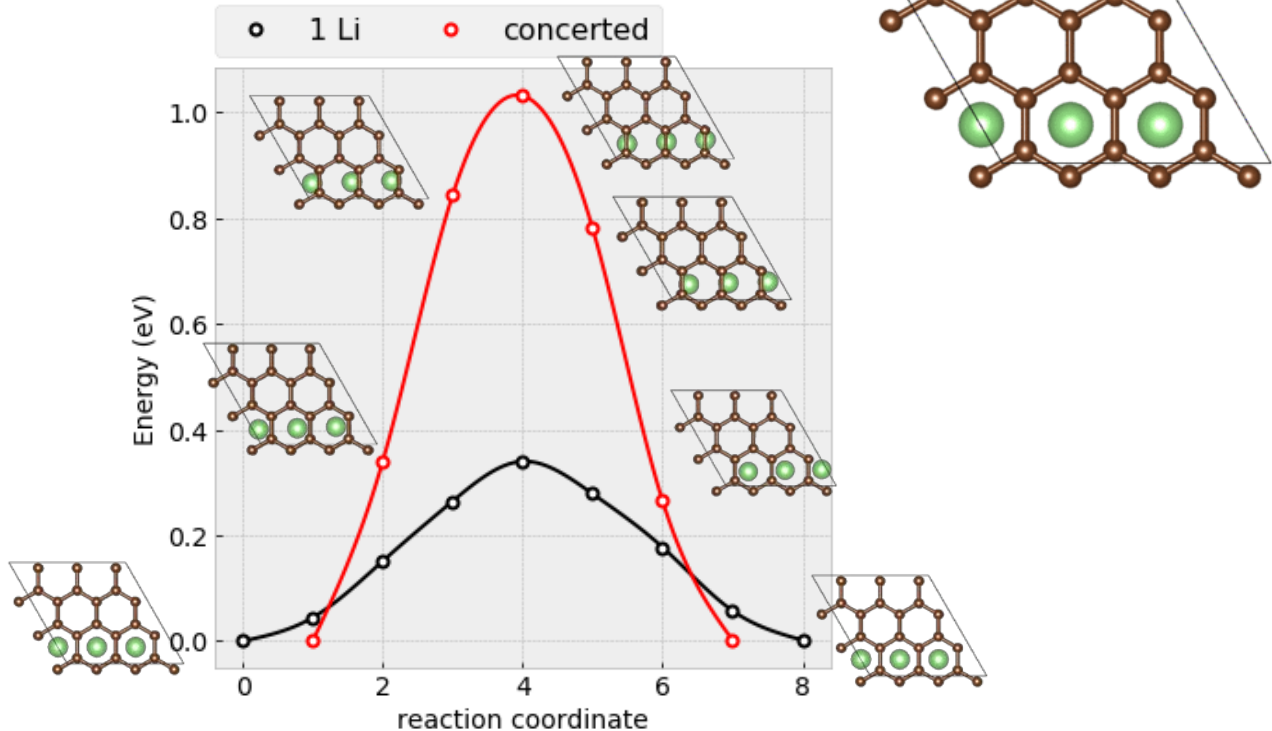
Neutral System

The energy barrier for Li diffusion is higher for concerted migration (translation mode):
Not favorable Li migration concentration profile

CONCERTED LI DIFFUSION

Neutral System

The energy barrier for Li diffusion is drastically reduced for concerted migration (concentration front: "asynchronous" mode): Increased Li diffusion coefficient

2) IMPACT OF HETEROGENEITIES ON LOCALIZED / EARLY ONSET OF LI PLATING

APPROACH – ELECTROCHEMICAL MODEL (BAT371) EXTENDED TO MULTIPLE LENGTH SCALES

…to quantify heterogeneity influences on localized/early onset of plating
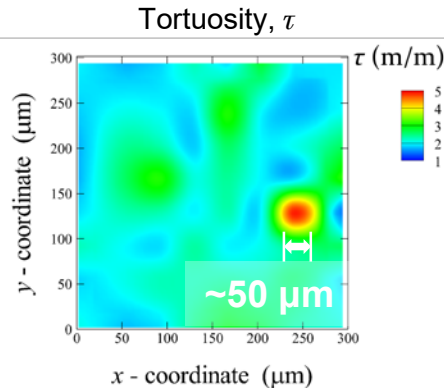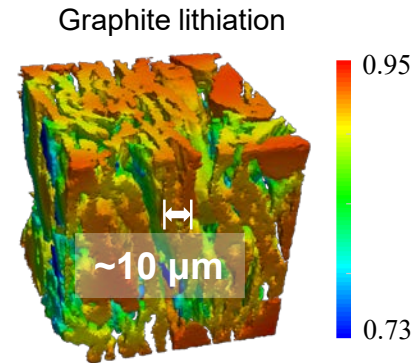
1) Edge effects

Round 2 cell aged at 6C
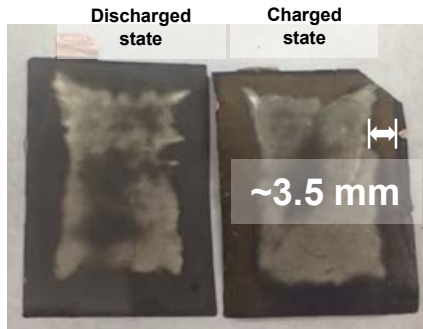
Photo: Eric Dufek and Tanvir Tanim, INL

- **2D electrochemical model** investigates why plating does not occur at edges

2) Coating heterogeneity

Tortuosity, τ

- **3D meso-scale model**

- **XCEL electrodes**: 3D electrode geometry imaged using micro- and nano-computed tomography

- **Virtual electrodes**: Stochastic reconstruction algorithms generate "what-if" geometries (BAT299)

3) Particle heterogeneity

Graphite lithiation


- **3D microstructure model**

MODELING OF ELECTRODE EDGE EFFECTS (1/2)

Anode overhangs cathode by 0.5 mm. Excess anode at edge (1) suppresses Li plating and (2) causes excessive cathode utilization
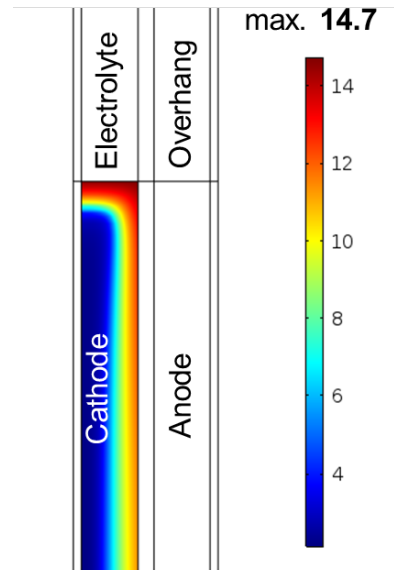
- 2D electrochemical model shows excessive C-rates in NMC at cathode edge on first 6C charge

- Damage model[1] relates NMC diffusivity to maximum C-rate

$$D_{s,\text{eff}} = \alpha\, D_{s,0}; \quad 0 < \alpha < 1$$

$$\alpha = (1 - f_{damage})^{\gamma}$$

max. **30.25**

$$\max[\text{C rate}(\boldsymbol{x}, t)]$$

max. **14.7**
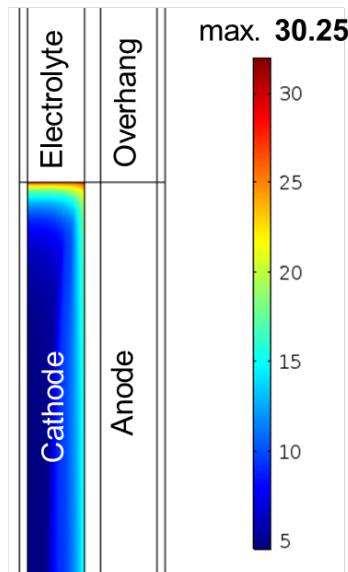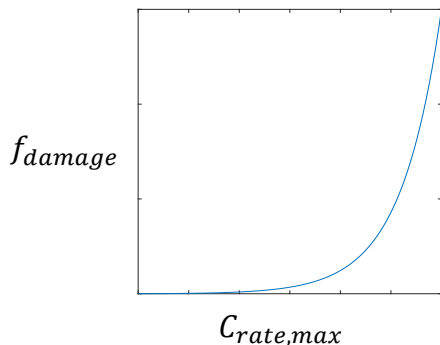
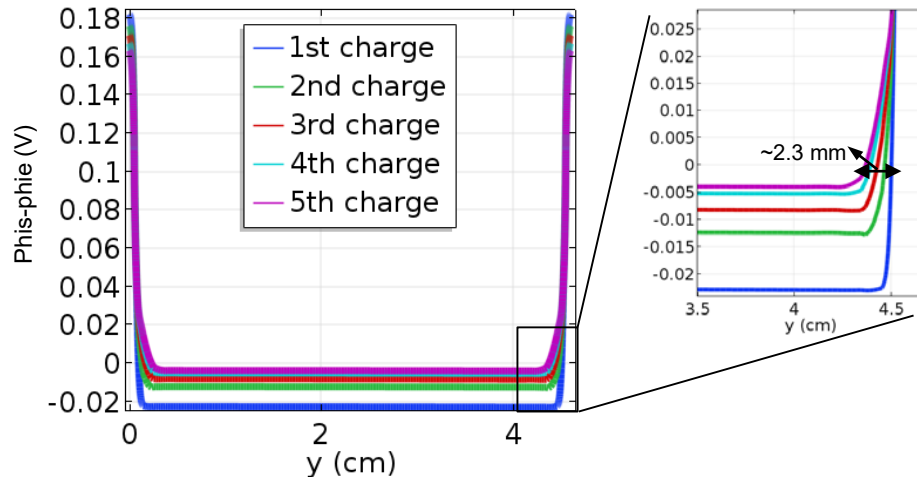$$\text{average}[\text{C rate}(\boldsymbol{x}, t)]$$

NMC: lithium nickel manganese cobalt oxide

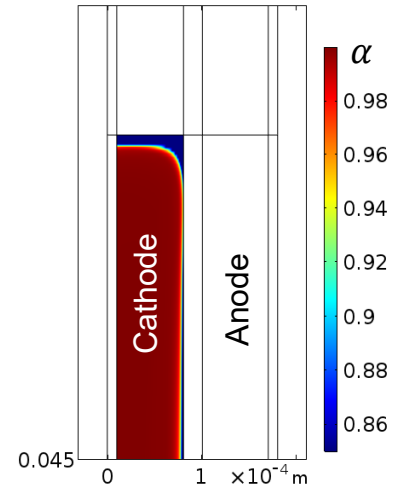1. Barai and Mukherjee. *J. Electrochem. Soc.* (2013)

MODELING OF ELECTRODE EDGE EFFECTS (2/2)

No plating zone increases from 1 mm to 2.3 mm over five cycles due to cathode damage. Explains localized Li plating in Round 2 cell.

Lithium plating potential at anode front surface
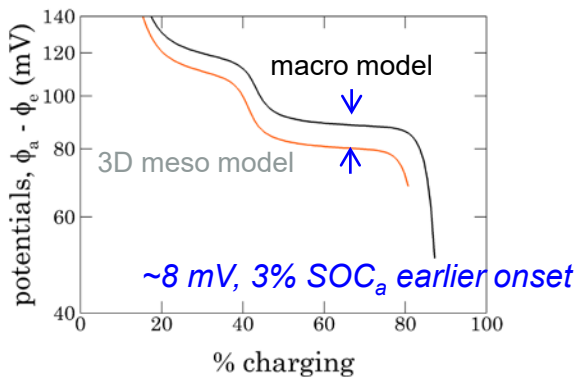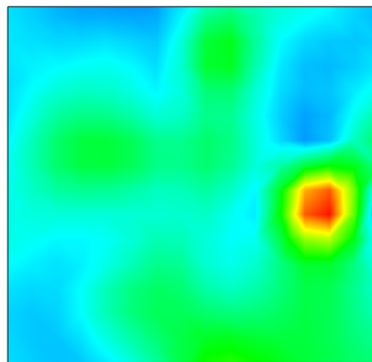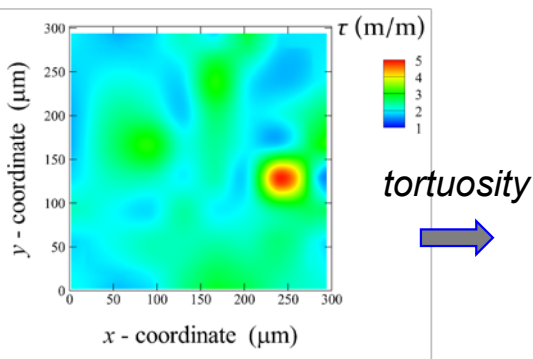
Cathode damage parameter, α

- Decreasing driving force for lithium plating due to increased negative-to-positive ratio and increased overpotential at cathode edges

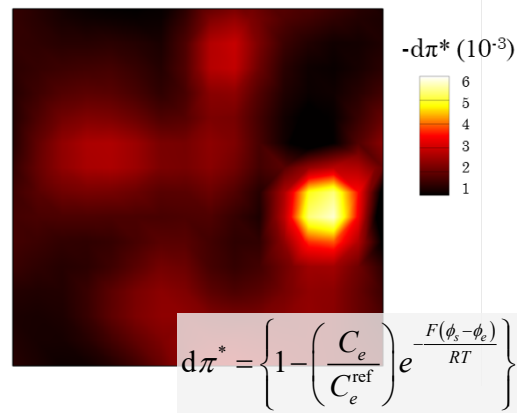- Damage evolution reaches steady state in around five cycles

ELECTRODE TORTUOSITY HETEROGENEITY

Computed tomography (CT) imaging of electrodes shows local regions with agglomeration of active material leading to high tortuosity and preferential Li plating.

τ (m/m)

ϕ_e (V)

tortuosity

electrolyte potential

Purdue University
Partha P. Mukherjee
Aashutosh Mistry

plating propensity

-dπ* (10^{-3})

macro model

3D meso model

~8 mV, 3% SOC$_a$ earlier onset

$$d\pi^* = \left\{ 1 - \left(\frac{C_e}{C_e^{\mathrm{ref}}} \right) e^{-\frac{F(\phi_s - \phi_e)}{RT}} \right\}$$

SOC$_a$: Anode state of charge

XCEL — eXtreme Fast Charge Cell Evaluation of Lithium-ion Batteries

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VEHICLE TECHNOLOGIES OFFICE
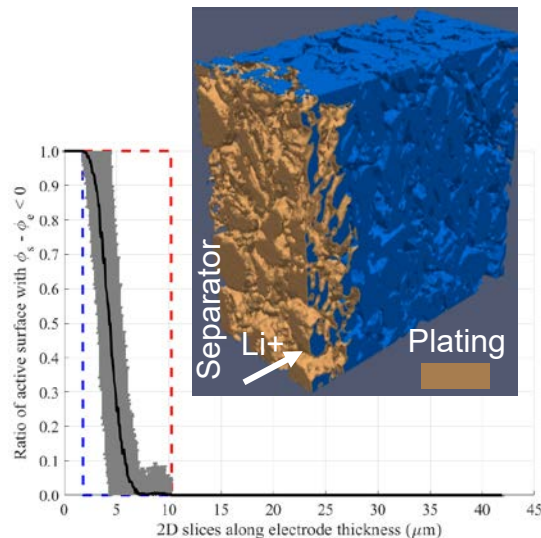
SLC1506T MICROSTRUCTURE HETEROGENEITY

At 6C, microstructure model predicts Li plating onset 2.5% anode SOC, 8 mV earlier than the macro-homogeneous model
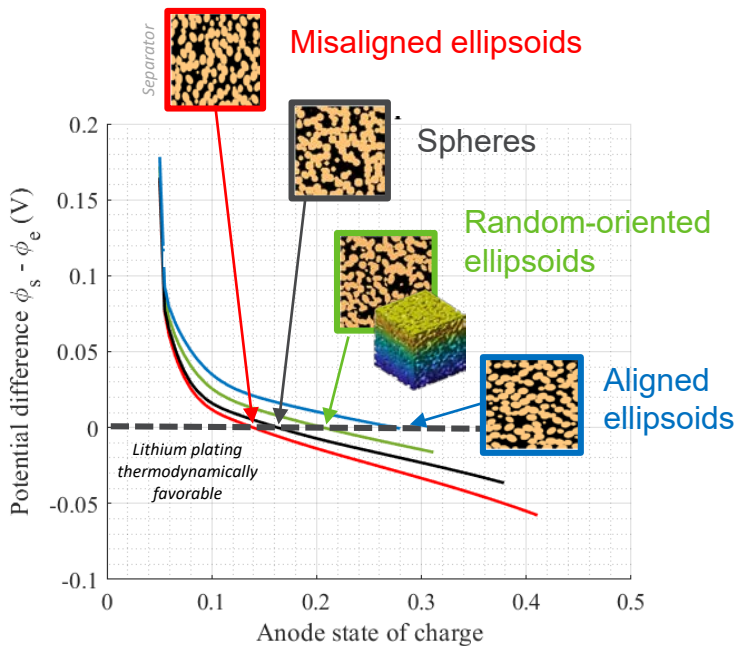

- Li plating front is ~8-µm thick
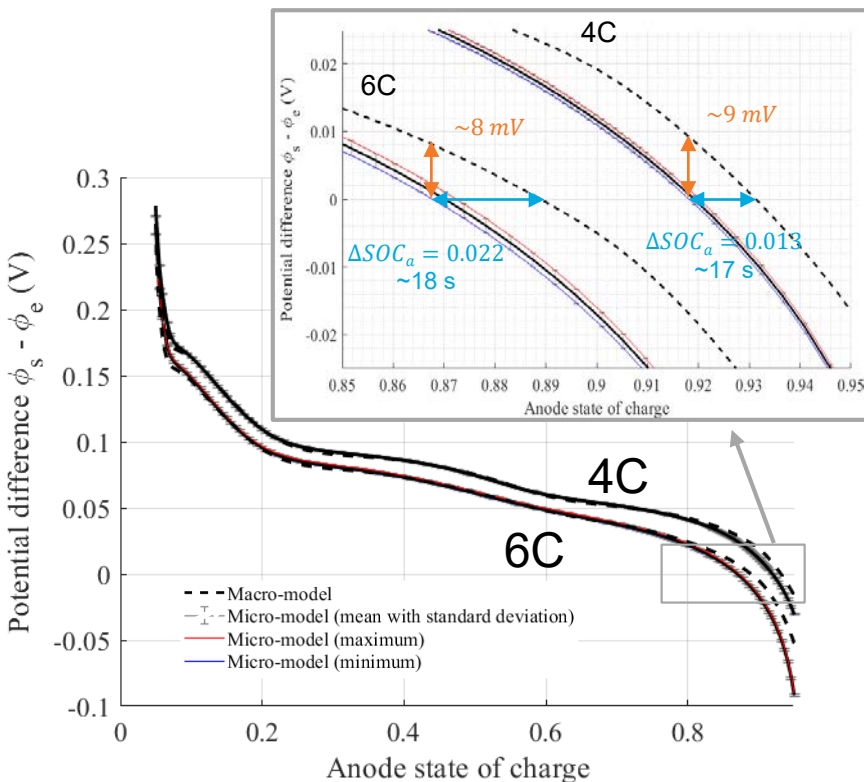
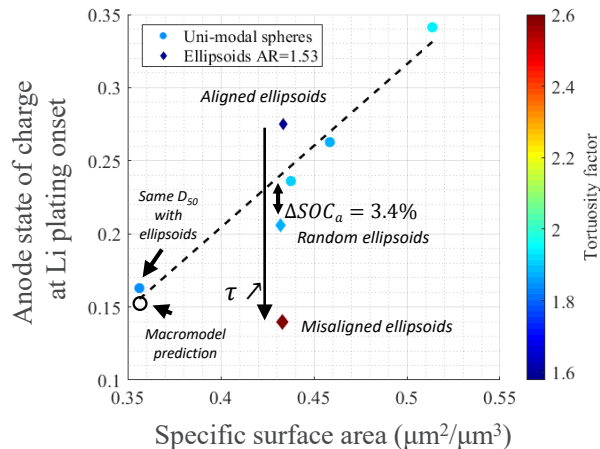SLC1506T Round1 electrode, 42-µm thick

PARTICLE MORPHOLOGY & ALIGNMENT IMPACT

## Electrode tortuosity and surface area are key variables controlling early Li plating

- Surface area is a more influential metric than particle size

- Higher surface area delays Li plating onset (though at some cost to calendar life)

- Low tortuosity also delays Li plating onset

$\langle \varepsilon \rangle = 0.4, \langle D_{50} \rangle = 7.8 \ \mu m, C_e = 400 \text{mol.m}^{-3}$,
6C, half cell domain $72 \times 72 \times (72 + 20) \ \mu m^3$

BI-MODAL PARTICLE DISTRIBUTION IMPACT
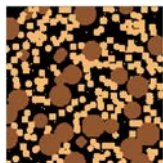
Bimodal

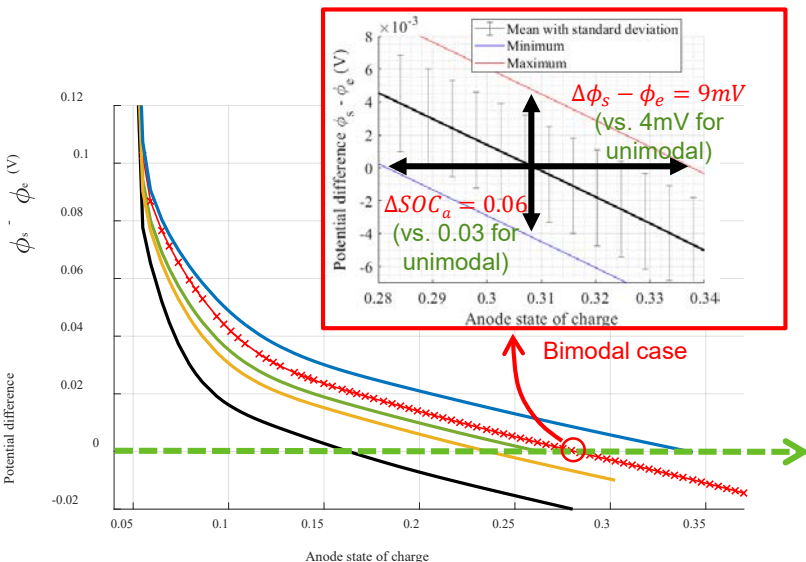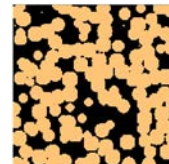$$D = \begin{bmatrix} 4.2\mu m & 7.8\mu m & 11.4\mu m \\ 50\% & 0\% & 50\% \end{bmatrix}$$

vs.

Unimodal

$D = 7.8\mu m$ (same D_{50}, lower S_p)
$D = 6.6\mu m$ (similar S_p)
$D = 6.3\mu m$ (similar S_p)
$D = 5.4\mu m$ (higher S_p)

$\phi_s - \phi_e$ (V)

Potential difference

Anode state of charge

Mean with standard deviation
Minimum
Maximum

$\Delta\phi_s - \phi_e = 9mV$
(vs. 4mV for unimodal)

$\Delta SOC_a = 0.06$
(vs. 0.03 for unimodal)

Potential difference $\phi_s - \phi_e$ (V)

Anode state of charge

Bimodal case

- Unimodal: Surface area differences explain differences in plating onset
- Bimodal plating:
  - 2.5%ΔSOC_a sooner than unimodal
  - Heterogeneity is 2x worse

Anode state of charge at Li plating onset

Specific surface area ($\mu m^2/\mu m^3$)

Unimodal cases

$\Delta SOC_a = 2.5\%$

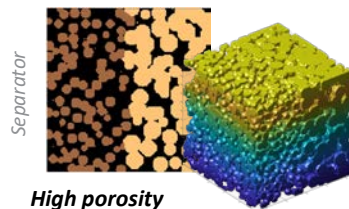Bimodal microstructure plates earlier

Uni-modal
Bi-modal
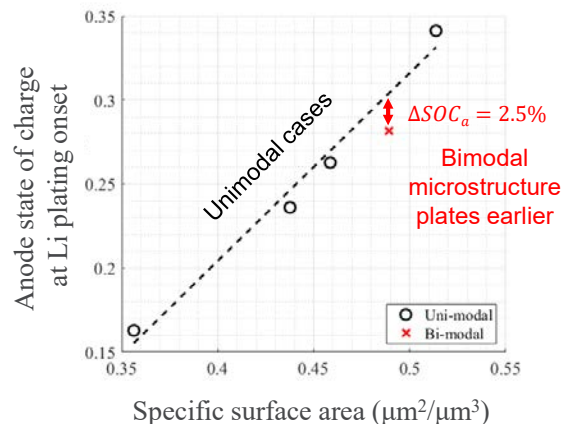
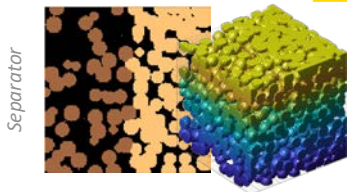*All microstructures have same porosity and tortuosity*

DUAL-COATED & GRADED ELECTRODE IMPACT

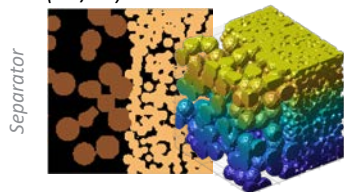**Combining high porosity and small particles near separator delays Li plating by 7% anode state of charge**

Porosity difference from front to back, $\Delta\varepsilon = 0.3$

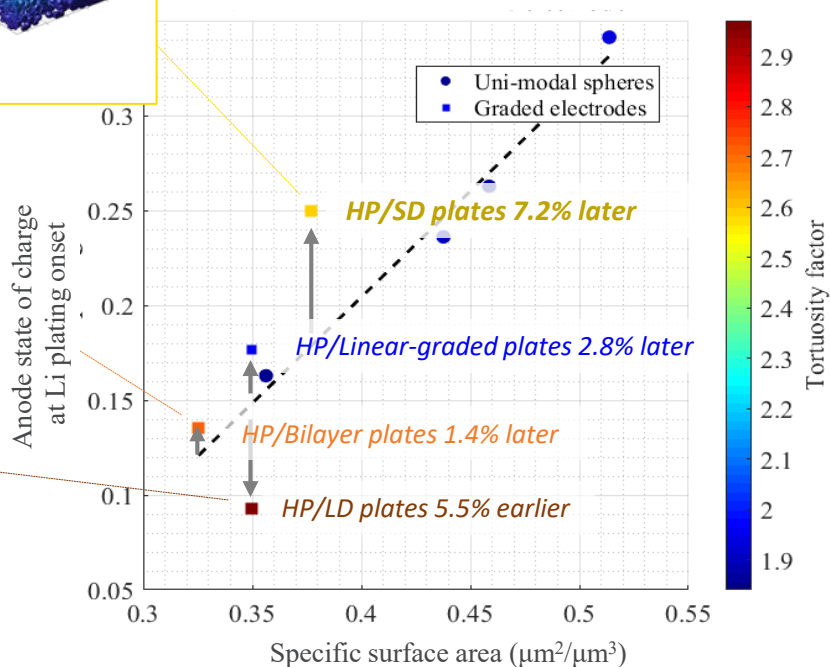*High porosity Small diameter (HP/SD)*

High porosity (HP/bilayer)

High porosity Large diameter (HP/LD)

- Dual/graded coatings provide slightly lower tortuosity
- Small particles near separator reduces surface overpotential & delays plating

HP/SD plates 7.2% later

HP/Linear-graded plates 2.8% later

HP/Bilayer plates 1.4% later

HP/LD plates 5.5% earlier

Uni-modal spheres
Graded electrodes

Anode state of charge at Li plating onset

Specific surface area ($\mu m^2/\mu m^3$)

Tortuosity factor

COLLABORATION ACROSS LABS AND UNIVERSITIES

Cell and electrode design and build, perf. characterization, post-test, cell and atomistic modeling, cost modeling

Li detection, electrode architecture, diagnostics

Performance characterization, Li detection, failure analysis, electrolyte modeling and characterization, acoustic detection

Li detection, novel separators, diagnostics

Thermal characterization, life modeling, micro and macro scale modeling, electrolyte modeling and characterization

- Purdue University – meso-scale modeling
- Univ. College London – computed tomography
- European Synchrotron (ESRF) – beamline experiments
- Univ. Oslo – beamline data reduction

RESPONSES TO PREVIOUS YEAR'S COMMENTS

- There are no previous year reviewer comments.

REMAINING CHALLENGES AND BARRIERS

- Large atomistic modeling system sizes are needed to extend the configuration space and include surface effects (computationally demanding)

- Li-plating heterogeneities are characterized by a large range of length-scales
  - Requires separate models to resolve
  - Difficulty in experimentally resolving Li plating at all length scales

PROPOSED FUTURE RESEARCH

- Compute energy barriers of Li diffusion when extra electrons are present in the system for different conditions (fixed cell, localized electrons, edges…)

- Investigate bulk defects, surface and edge effects for select cases

- Apply Kinetic Monte Carlo simulations to predict changes in diffusion coefficient under fast charging

- Continue to improve the fidelity of multi-scale electrochemical models to
  - Explain experimental findings
  - Develop electrode/cell design guidelines

- Investigate subparticle- and cell-scale heterogeneities

- Predictive modeling of aging due to fast charge and mitigation strategies

Any proposed future work is subject to change based on funding levels

SUMMARY

1) Atomistic modeling

- During fast charge, non-equilibrium conditions can induce extra negative local charge accumulation near the anode surface, which can lead to increased graphite spacing, and hence increased Li diffusion coefficient (lower Li migration barriers)

- The staging sequence might be altered as a consequence of graphite spacing response to local non-equilibrium conditions

- Concerted Li diffusion states affect Li diffusion coefficients

2) Impact of heterogeneities on Li plating

- 2D edge effects explain localized Li plating in center of Round 2 cells

- Coating and microstructure heterogeneities lead to $5\%\Delta SOC_a$ early plating onset

- Best (single-coated) electrode
  - Low tortuosity (spherical particles… or platelets/ellipsoids if aligned in thru-plane direction)
  - High surface area (with limit determined by calendar life-limiting side reactions)
  - Homogenous particle size

- Dual-coated electrode – delays plating by $7\%\Delta SOC_a$ under electrolyte-limited situations
  - Back: low porosity, large particles
  - Front: high porosity, small particles

CONTRIBUTORS AND ACKNOWLEDGEMENTS

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Andrew Colclasure
Antony Vamvakeros
Aron Saxon
Bryan McCloskey
Bryant Polzin
Chuntian Cao
Daniel Abraham
Daniel Steingart
Dave Kim
David Robertson
David Wragg
Dean Skoien
Dennis Dees
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Eongyu Yi
Eric Dufek
Francois Usseglio-Viretta
Francesco De Carlo
Guoying Chen
Hakim Iddir
Hans-Georg Steinrück

Hansen Wang
Ilya Shkrob
Ira Bloom
Jiayu Wan
Jianming Bai
Johanna Nelson Weker
John Okasinski
Juan Garcia
Kamila Wiaderek
Kandler Smith
Kaushik Kalaga
Kevin Gering
Marca Doeff
Marco DiMichiel
Marco Rodrigues
Matt Keyser
Michael Evans
Michael Toney
Nancy Dietz Rago
Nitash Balsara
Olaf Borkiewicz
Partha Mukherjee
Partha Paul
Paul Shearing
Pavel Shevchenko

Pierre Yao
Ravi Prasher
Ren Yang
Robert Kostecki
Ruqing Xu
Ryan Jackman
Sang Cheol Kim
Sangwook Kim
Sean Wood
Seoung-Bum Son
Shabbir Ahmed
Shriram Santhanagopalan
Steve Trask
Tanvir Tanim
Uta Ruett
Venkat Srinivasan
Victor Maroni
Vince Battaglia
Vivek Thampy
Wei Tong
Weijie Mai
Wenxiao Huang
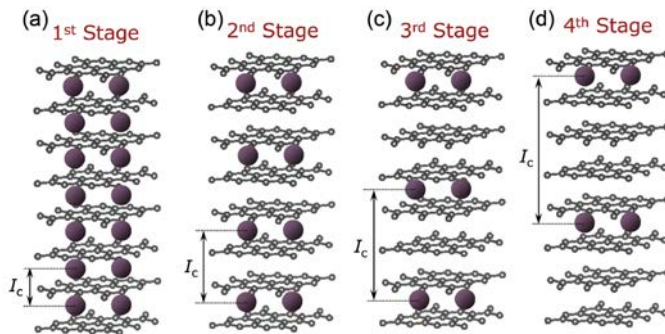William Huang
Yanying Zhu
Yi Cui

Zhenzhen Yang

TECHNICAL BACK-UP SLIDES

GRAPHITE STAGING DURING CHARGE

Staging structure of C_6Li_x: (a) first-stage for C_6Li, (b) second-stages for $C_{12}Li$ and $C_{18}Li$, (c) third-stage for $C_{27}Li$, and (d) fourth-stage for $C_{36}Li$.

- Staging follows a thermodynamically favored phase transformation.
- 4th stage is the most favorable initial stage.

Mukai and Inoue. *Carbon* 123 (2017) 645-650
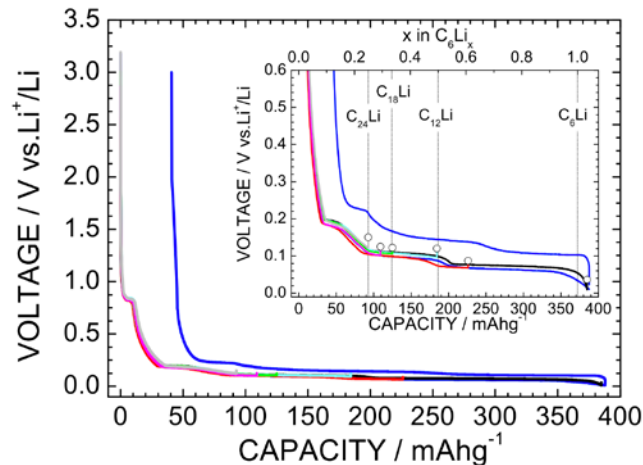
Discharge and charge curves of the graphite/Li cells for seven C_6L_{ix} samples. The applied current was 0.3 mA, which corresponds to a current density of ~0.096 mA cm^2 based on the surface area of the NG electrode.

GRAPHITE INTER-PLANAR DISTANCE DURING FAST CHARGING
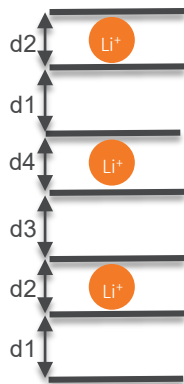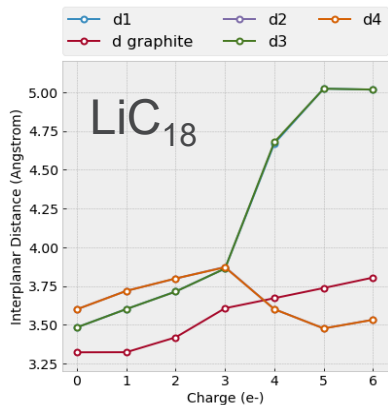
- LiC_{18} with extra electrons also favor the filling of adjacent empty channels before going to LiC_{12}

- Even after the formation of LiC_{12} the increased inter-planar distance would speed up the formation of LiC_6
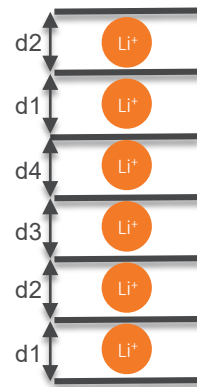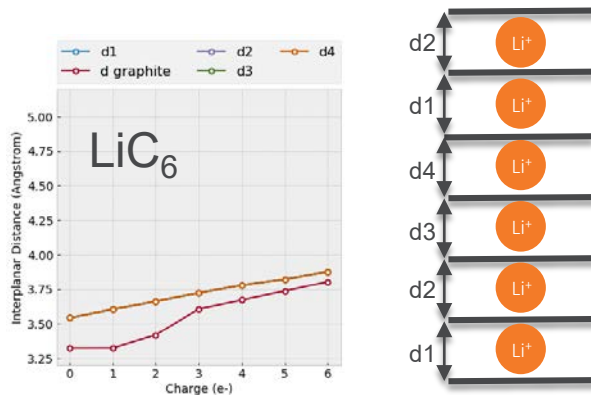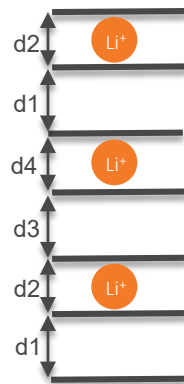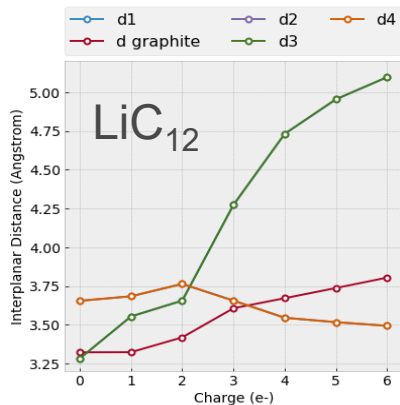
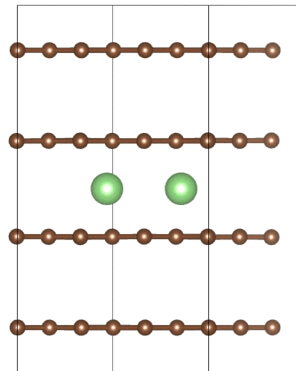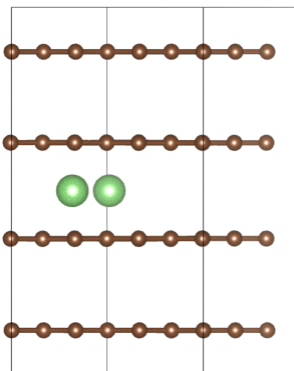# Electron density differences with extra electrons in the simulation box

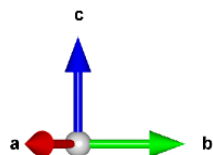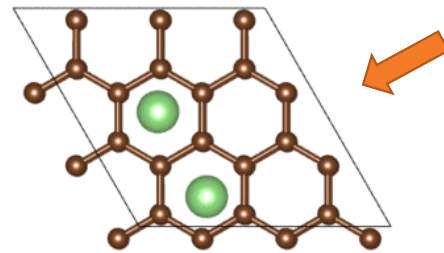| No extra electrons	Three extra electrons	Six extra electrons
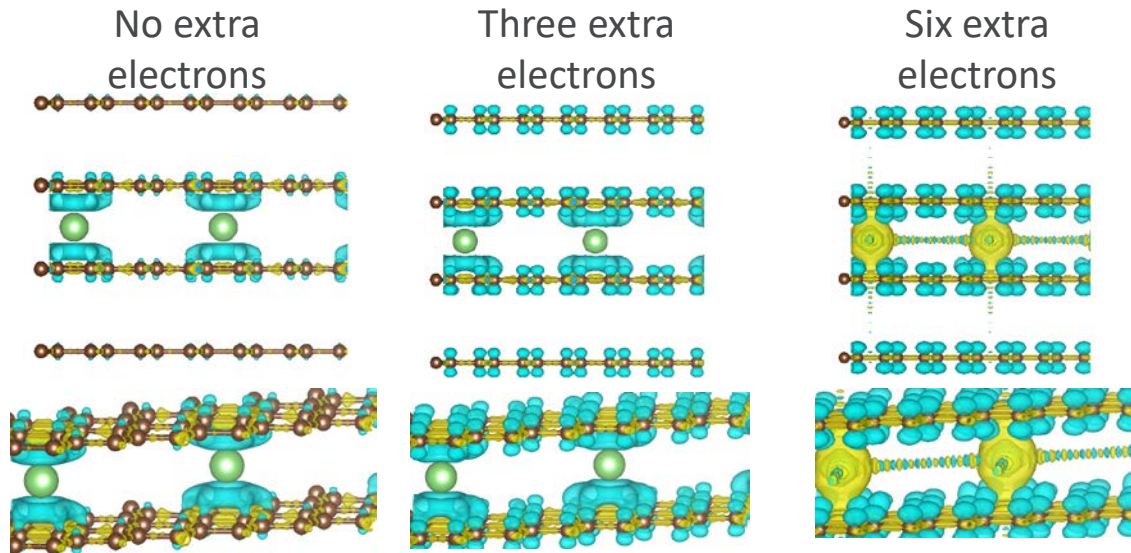
The blue iso-surfaces represent regions where the electron difference is positive (extra electron density gain). The yellow iso-surfaces represent regions with a negative electron density difference (charge depletion).

- Electrons were withdrawn from the sp2 hybridized orbital within the graphene layer, as shown in iso-surfaces (yellow)
- The charge density redistribution is such that the extra charge is pointing away from the graphene planes (P_z orbitals), increasing the electrostatic repulsion between the layers.
- For six extra electrons, the Li ions show a purely ionic character that would strongly attract the carbon layers adjacent to them, reducing the interlayer spacing between the Li-occupied graphite layers

XCEL
eXtreme Fast Charge Cell Evaluation of Lithium-ion Batteries

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy
VEHICLE TECHNOLOGIES OFFICE

Concerted Li diffusion
Neutral System
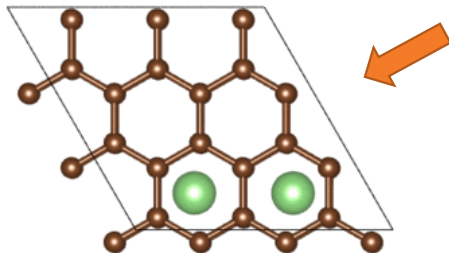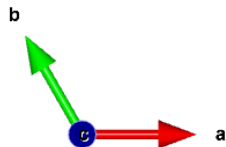
SUMMARY OF GRADED ARCHITECTURES INVESTIGATED WITH MICROSTUCTURE MODEL

Graded architecture investigated	Impact on Li plating $\varepsilon = 0.4$ and similar average specific surface area
High porosity/Large diameter (HP/LD) Low porosity/Small diameter	plate earlier (Li$_x$ -0.055) with larger tortuosity
High porosity – low porosity	plate later (Li$_x$ +0.014) with larger tortuosity
Linear porosity variation	plate later (Li$_x$ +0.028) with similar tortuosity
High porosity/Small diameter (HP/SD) Low porosity/Larger diameter	plate later (Li$_x$ +0.072) with larger tortuosity

Particle heterogeneity investigated	Impact on Li plating $\varepsilon = 0.4$ and similar tortuosity factor (~1.8)
Bi-modal distribution particle size	• At similar average particle size: plate later (Li$_x$ +0.12) • At similar specific surface area: Plate earlier (Li$_x$ -0.023)
Non-spherical particles (ellipsoid with random orientation)	• At similar average particle size: plate later (Li$_x$ +0.042) • At similar specific surface area: Plate earlier (Li$_x$ -0.034)

- Combining porosity and particle size variation seems to be the best option for suppressing Li plating

- These different particle heterogeneity contributions to lithium plating are combined for actual electrodes and are a source of underestimation for macro-homogenous model

DUAL-COATED ELECTRODE IMPACT

Combining high porosity and small particles (HP/SD) near separator delays Li plating

- This benefit is most pronounced for electrolyte transport-limited designs like that shown[1 at right]

- If electrolyte transport is enhanced (low tortuosity architectures, elevated temperature, next generation electrolyte), plating occurs later in charge and the benefit largely goes away[2 at right]

- Optimization study required to identify optimal dual-coated design parameters ($\Delta\varepsilon, \Delta D_{50}$, layer thickness ratio) to keep benefit over wider operating conditions

$\langle\varepsilon\rangle = 0.4, \langle D_{50}\rangle = 7.8\ \mu m, C_e = 400\text{mol.m}^{-3}$,
$6C$, half cell domain $72 \times 72 \times (72 + 20)\ \mu m^3$

Potential difference at the separator-anode interface

Legend:
- Reference (uni-modal, non graded)
- Graded porosity (linear slope)
- Graded porosity (bi-layer)
- Graded porosity and particle size (bi-layer) HP/SD-LP/LD
- Graded porosity and particle size (bi-layer) HP/LD-LP/SD

Potential difference $\phi_s - \phi_e$ (V)

Anode state of charge

Lithium plating favorable condition